

<b>Office Action Summary</b>	<b>Application No.</b> 10/088,980	<b>Applicant(s)</b> HATCHMAN ET AL.	
	<b>Examiner</b> Daniel S. Metzmaier	<b>Art Unit</b> 1712	

-- The MAILING DATE of this communication appears on the cover sheet with the correspondence address --

**Period for Reply**

A SHORTENED STATUTORY PERIOD FOR REPLY IS SET TO EXPIRE 3 MONTH(S) OR THIRTY (30) DAYS, WHICHEVER IS LONGER, FROM THE MAILING DATE OF THIS COMMUNICATION.

- Extensions of time may be available under the provisions of 37 CFR 1.136(a). In no event, however, may a reply be timely filed after SIX (6) MONTHS from the mailing date of this communication.
- If NO period for reply is specified above, the maximum statutory period will apply and will expire SIX (6) MONTHS from the mailing date of this communication.
- Failure to reply within the set or extended period for reply will, by statute, cause the application to become ABANDONED (35 U.S.C. § 133). Any reply received by the Office later than three months after the mailing date of this communication, even if timely filed, may reduce any earned patent term adjustment. See 37 CFR 1.704(b).

**Status**

- 1) ☒ Responsive to communication(s) filed on 17 August 2006.
- 2a) ☐ This action is **FINAL**.                      2b) ☒ This action is non-final.
- 3) ☐ Since this application is in condition for allowance except for formal matters, prosecution as to the merits is closed in accordance with the practice under *Ex parte Quayle*, 1935 C.D. 11, 453 O.G. 213.

**Disposition of Claims**

- 4) ☒ Claim(s) 1-6 is/are pending in the application.
- 4a) Of the above claim(s) \_\_\_\_\_ is/are withdrawn from consideration.
- 5) ☐ Claim(s) \_\_\_\_\_ is/are allowed.
- 6) ☒ Claim(s) 1-6 is/are rejected.
- 7) ☐ Claim(s) \_\_\_\_\_ is/are objected to.
- 8) ☐ Claim(s) \_\_\_\_\_ are subject to restriction and/or election requirement.

**Application Papers**

- 9) ☐ The specification is objected to by the Examiner.
- 10) ☐ The drawing(s) filed on \_\_\_\_\_ is/are: a) ☐ accepted or b) ☐ objected to by the Examiner.  
Applicant may not request that any objection to the drawing(s) be held in abeyance. See 37 CFR 1.85(a).  
Replacement drawing sheet(s) including the correction is required if the drawing(s) is objected to. See 37 CFR 1.121(d).
- 11) ☐ The oath or declaration is objected to by the Examiner. Note the attached Office Action or form PTO-152.

**Priority under 35 U.S.C. § 119**

- 12) ☐ Acknowledgment is made of a claim for foreign priority under 35 U.S.C. § 119(a)-(d) or (f).
- a) ☐ All    b) ☐ Some \*    c) ☐ None of:
1. ☐ Certified copies of the priority documents have been received.
2. ☐ Certified copies of the priority documents have been received in Application No. \_\_\_\_\_.
3. ☐ Copies of the certified copies of the priority documents have been received in this National Stage application from the International Bureau (PCT Rule 17.2(a)).

\* See the attached detailed Office action for a list of the certified copies not received.

**Attachment(s)**

- |  |   |
|--|---|
| 1) <input checked="" type="checkbox"/> Notice of References Cited (PTO-892)  | 4) <input type="checkbox"/> Interview Summary (PTO-413)<br>Paper No(s)/Mail Date. _____ |
| 2) <input type="checkbox"/> Notice of Draftsperson's Patent Drawing Review (PTO-948)                                   | 5) <input type="checkbox"/> Notice of Informal Patent Application (PTO-152)             |
| 3) <input type="checkbox"/> Information Disclosure Statement(s) (PTO-1449 or PTO/SB/08)<br>Paper No(s)/Mail Date _____ | 6) <input type="checkbox"/> Other: _____  |

### **DETAILED ACTION**

Claims 1-6 are pending.

#### ***Continued Examination Under 37 CFR 1.114***

1. A request for continued examination under 37 CFR 1.114, including the fee set forth in 37 CFR 1.17(e), was filed in this application after final rejection. Since this application is eligible for continued examination under 37 CFR 1.114, and the fee set forth in 37 CFR 1.17(e) has been timely paid, the finality of the previous Office action has been withdrawn pursuant to 37 CFR 1.114. Applicant's submission filed on 23 May 2006 and 17 August 2006 have been entered. The 17 August 2006 amendment appears to be a duplicate of the submission filed on 23 May 2006. The 17 August 2006 remarks have been addressed.

#### ***Claim Rejections - 35 USC § 112***

2. The following is a quotation of the second paragraph of 35 U.S.C. 112:

The specification shall conclude with one or more claims particularly pointing out and distinctly claiming the subject matter, which the applicant regards as his invention.

3. Claims 1-3 are rejected under 35 U.S.C. 112, second paragraph, as being indefinite for failing to particularly point out and distinctly claim the subject matter which applicant regards as the invention. Claims 1-3 are indefinite since the surfactant and the electrolyte components overlap for anionic, amphoteric and cationic surfactants. It is unclear what extent one skilled in the art should attribute materials to the concentration range set forth in the claims as surfactant and electrolyte for anionic, amphoteric and cationic surfactants, since said surfactants dissociate in aqueous solution forming electrolytes.

***Claim Rejections - 35 USC § 102***

4. The following is a quotation of the appropriate paragraphs of 35 U.S.C. 102 that form the basis for the rejections under this section made in this Office action:

A person shall be entitled to a patent unless –

(b) the invention was patented or described in a printed publication in this or a foreign country or in public use or on sale in this country, more than one year prior to the date of application for patent in the United States.

5. Claim 1-3 is rejected under 35 U.S.C. 102(b) as being anticipated by Lion Corp, DE 36 17 306 A (hereafter Lion), as evidenced by Derwent Abstract AN 1986-320274. Lion (claims 1, 3, and 4; page 5, lines 34, to page 6, line 17; page 7, line 26, to page 8, line 7; page 9, lines 4-6; page 10, line 33, to page 11, line 15; page 12, lines 7, to page 14, line 15; example 1; table III; page 18, lines 1-19; examples 19, 20; table IV; and Derwent Abstract) discloses pearlescent concentrates employing ethylene glycol distearate, anionic sulfates, and coemulsifiers and characterizes said compositions as having an isotropically clear phase enabling the pearly luster appearance (see Derwent Abstract). The disclosed compositions would have inherently provided the protolamellar structure based on the components and the characterization of the compositions as lamellar and providing an excellent pearly luster in the concentrate.

Further attention is directed to Table III, example 1, which sets forth 30 parts ethylene glycol distearate, 45 parts LES-Na and 4 parts potassium chloride. Said example reads on the claims. It is noted that claims 1-3 provide for only the concentration of the electrolyte.

***Claim Rejections - 35 USC § 103***

6. The following is a quotation of 35 U.S.C. 103(a) which forms the basis for all obviousness rejections set forth in this Office action:

(a) A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negated by the manner in which the invention was made.

7. This application currently names joint inventors. In considering patentability of the claims under 35 U.S.C. 103(a), the examiner presumes that the subject matter of the various claims was commonly owned at the time any inventions covered therein were made absent any evidence to the contrary. Applicant is advised of the obligation under 37 CFR 1.56 to point out the inventor and invention dates of each claim that was not commonly owned at the time a later invention was made in order for the examiner to consider the applicability of 35 U.S.C. 103(c) and potential 35 U.S.C. 102(e), (f) or (g) prior art under 35 U.S.C. 103(a).

8. Claims 3-6 are rejected under 35 U.S.C. 103(a) as being unpatentable over Horiuchi et al, US 4,486,334, in view of Hawkins, US 5,952,285, and Albright & Wilson LTD, AU-A-16451/95.

Horiuchi et al (abstract, examples, and claims) disclose aqueous pearlescent concentrate compositions comprising 3 to 45 wt% of a pearlizing agent including ethylene glycol distearate, and 30 to 50 wt% of sodium polyoxyethylene lauryl ether sulfate as a middle phase ( $M_1$  phase) liquid crystals. Horiuchi et al (column 3, lines 46 et seq; examples; and claims) discloses the formation of the middle phase liquid crystals by dispersing the pearlescent agent above the melting point (i.e., 50 to 80° C)

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followed by cooling to form the pearlizing agent. Horiuchi et al (column 4, lines 6 et seq) further teaches the specific surfactant concentration can be determined by the limitation of the pearlizing agents, which can be solubilized in the micelles at a concentration of 3 to 45 wt% of pearlizing agent.

Horiuchi et al differs from the claims in the further addition of a simple salt electrolyte (e.g., NaCl), an explicit disclosure of the pearlizer particle size and the particular concentration ranges claimed.

Hawkins (abstract; column 7, lines 54 et seq) discloses the addition of electrolyte to middle phase liquid crystalline ((hexagonal or cubic symmetry) resulting in an pourable optically isotropically liquid composition. Hawkins (column 20, lines 6-10; and column 24, Table II) teaches chloride salts and exemplifies 1 wt% of sodium chloride.

Hawkins (column 17, lines 29 et seq) further teaches increasing the cloud point of surfactants by the addition of small amounts of sodium chloride.

Albright & Wilson further teach the formation of pearlescent concentrate compositions. Albright & Wilson (page 2 and examples) discloses ethylene glycol mono- and distearate mixtures as pearlizing agents. Albright & Wilson (claims 14 and 15 and figures) discloses the particles size for said pearlizing agents in the suspensions are that at least 90% of the particles are 5 to 20 microns.

These references are combinable because they teach surfactant compositions having liquid crystalline structures and modifications thereof by varying concentrations and materials. It would have been obvious to one of ordinary skilled in the art at the time of applicants' invention to add sufficient sodium chloride to the compositions of

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Horiuchi et al for the advantage of forming an optically isotropically liquid composition and the added advantage of handling ease esthetic appearance of the concentrates.

The particles sizes would have been obvious to one of ordinary skilled in the art at the time of applicants' invention as conventional sizes shown in the Albright & Wilson reference. It would have been obvious to one of ordinary skilled in the art at the time of applicants' invention to vary the concentrations as a point of law. See also MPEP 2144.05(I) wherein it sets forth, "A *prima facie* case of obviousness exists where the claimed ranges and prior art ranges do not overlap but are close enough that one skilled in the art would have expected them to have the same properties. ***Titanium Metals Corp. of America v. Banner***, 778 F.2d 775, 227 USPQ 773 (Fed. Cir. 1985)."

9. The remaining references cited in the search report as X references for claims 1-3 are considered cumulative to the references relied on in the above rejections over claim 3 or 3-6, respectively.

### ***Response to Arguments***

10. Applicant's arguments filed August 17, 2006 have been fully considered but they are not persuasive.

Applicants (page 4) assert Lion as evidenced by Derwent '274 lacks a recitation of a protolamellar phase. This has not been deemed persuasive since the Lion compositions comprise isotropic compositions that otherwise read on the claims. Since a compound or composition and all of its properties are generally inseparable, (***In re Papsech***, 315 F2d. 381, 137 USPQ 43, (CCPA 1963)) said property would have been expected in the claimed compositions. Applicants characterize the isotropic character

as an indication of protolamellar properties. Attention is directed to page 2, 2<sup>nd</sup> full paragraph of the instant specification.

Applicants (page 6) assert the inventive compositions are clear and optically isotropic. The Derwent '274 states the Lion material has good pearly lustre without the need for a separate crystallization step.

11. Applicants further (page 4) assert the Lion reference fails to disclose the wetting agent as a surfactant. Attention is specifically directed to the definition of "wetting agent", "surface-active agent", and "surfactant" as set forth in Hawley's Condensed Chemical Dictionary, pages 1111-1112 and 1235. Please note that "wetting agent" is defined as a "surface-active agent", i.e., "surfactant".

Furthermore, example 1 (Table III, page 16) of the Lion reference sets forth LES-Na as the surface-active wetting agent and (page 15) denotes said compound as sodium polyoxyethylene lauryl ether sulfate with 3 moles of ethylene oxide added. Attention is further directed to Myers, Surfactant Science and Technology, 2<sup>nd</sup> Ed, pages 46-47, wherein the alcohol ether sulfates (AES) are specifically characterized as surfactants.

Applicants further (pages 4 and 5) assert the Lion reference contemplates the use of alcohol as the wetting agent, which applicants assert would not work to form the liquid crystalline phase. It is unclear what basis applicants rely for their assertion that alcohol is employed as a wetting agent. While the Lion reference (page 8, lines 9-12) does disclose the use of nonionic surfactants as wetting agents, it is unclear where the

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Lion reference specifically discloses alcohols per se. The Lion reference does disclose pearlizing agents, which are ester-alcohols.

Furthermore, any alleged disclosure of alcohols is not deemed persuasive in view of the facts that: (1) since the agent is disclosed as a wetting agent, (2) wetting agents are defined as surfactants, and (3) the claims are directed to the use of surfactants; it is logical to conclude any alleged or disclosed alcohols must be surfactants.

One having ordinary skill in the art does not view the prior art in a vacuum or without the knowledge that forms the state of the art. Furthermore, attention is directed to Horiuchi et al (column 3, line 15 et seq; example 2; column 5, lines 58-59), which employs AES as a surfactant and more specifically mentions the same compound as LES-Na employed in Lion.

12. Applicants (page 5 and 6) assert there exist no motivation to employ the teachings of Hawkins in the methods of the Horiuchi et al reference. Applicants further assert Hawkins adds the electrolyte to breakdown structure. Applicants conclude one of ordinary skill in the art would not combine Hawkins with the Horiuchi et al reference to build structure. This has not been deemed persuasive for the following reasons:

(1) Initially, it is unclear how applicants reach a conclusion that the abstract of Hawkins teaches the break down of structure. Hawkins abstract sets forth:

A liquid detergent composition containing water; surfactant in a concentration which would in the absence of electrolyte forms a pourable hexagonal, or cubic phase at 20.degree. C.; and sufficient dissolved electrolyte to form a substantially Newtonian or optically isotropic liquid.



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Hawkins employs the well-known effect of electrolyte addition to increase solubility of the internal phase of micelles and reduce the critical micelle concentration (CMC) of the surfactants. Attention is further directed to Myers, Surfactant Science and Technology, 2<sup>nd</sup> Ed, pages 119-120, wherein the presence of electrolytes in aqueous surfactant solutions reduces the CMC and said effect is greater for ionic surfactants. See also, Rosen, Surfactants and Interfacial Phenomena, pages 131-132. Attention is directed to the instant specification at page 4, 3<sup>rd</sup> full paragraph, wherein the preferred, surfactants are anionic, i.e., ionic surfactants.

(2) While the addition of electrolyte may be characterization as breaking one structure (e.g., hexagonal or cubic phase), it can likewise be characterized as the formation of optically isotropic liquids (e.g., protolamellar). See the instant specification at page 2, 2<sup>nd</sup> full paragraph, where the protolamellar solutions are characterized as optically isotropic liquids.

(3) Hawkins (abstract) discloses the formation of optically isotropic liquids. Applicants characterize (page 2, 2<sup>nd</sup> ¶) the protolamellar solutions are optically isotropic liquids.

(4) Lastly, attention is directed to paragraphs denoted "11.", including items (1) through (5), pages 7-9, Office Action mailed March 23, 2006, which discuss the term "protolamellar" and are incorporated herein by reference.

13. Applicants (page 6) assert the higher concentrations of surfactant with electrolyte would result in high viscosity LC phases unaffected by electrolyte. Applicants conclude any other conclusion based on Hawkins and Horiuchi et al is based on hindsight. This

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has not been deemed persuasive since at least claim 4 includes 30 % by weight of surfactants.

Furthermore, the addition of electrolyte is known to decrease the CMC of ionic surfactants. It would have been obvious to one having ordinary skill in the art at the time of the invention to employ lower concentrations of surfactants with a reasonable expectation of success since: (1) the addition of electrolyte is known to decrease the CMC of ionic surfactants, (2) applicants prefer ionic and more specifically anionic surfactants, (3) Hawkins clearly teaches (column 17 and 18, examples and claim 2) lower surfactant concentrations in the presence of electrolyte, and (4) the claims do not define a viscosity element and thus, the arguments are not commensurate in scope with the claims.

In response to applicant's argument that the examiner's conclusion of obviousness is based upon improper hindsight reasoning, it must be recognized that any judgment on obviousness is in a sense necessarily a reconstruction based upon hindsight reasoning. But so long as it takes into account only knowledge which was within the level of ordinary skill at the time the claimed invention was made, and does not include knowledge gleaned only from the applicant's disclosure, such a reconstruction is proper. See *In re McLaughlin*, 443 F.2d 1392, 170 USPQ 209 (CCPA 1971).

14. Applicants (page 6) assert Albright & Wilson is improperly combined with Horiuchi et al and Hawkins since (page 2, lines 3-7) disclose the desire to exclude salt. This has not been deemed persuasive for the following reasons. See MPEP 2141.01.

A reference may be combinable if it is "analogous prior art". Analogous prior art is "in the field of applicant's endeavor" or "reasonably pertinent to the particular problem with which the inventor was concerned". Applicants field of endeavor is the formation of "stable systems for suspending pearling concentrates for incorporation into liquid formulations such as shampoos and toiletries to impart a nacreous iridescence". See instant specification, page 1, first paragraph. Albright & Wilson are directed to pearlescent concentrates for use in cosmetic, hair, washing, shower preparations. See page 1, first paragraph of Albright & Wilson.

Furthermore, Albright & Wilson is cited only to show the conventional pearling agent particle sizes. Applicants do not dispute that the particle size of the pearling agents shown in Albright & Wilson to be conventional nor that the addition combination of Horiuchi et al and Hawkins somehow would destroy said particle size.

Applicants (pages 6 and 7) further assert the Albright & Wilson reference teaches high concentrations of surfactants. Applicants have not shown said concentrations to have an effect on the particle size of the pearling agent, which is employed in the same or substantially the same concentrations.

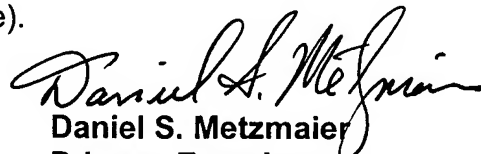
In response to applicant's argument that the examiner's conclusion of obviousness is based upon improper hindsight reasoning, Said argument has been addressed above. See *In re McLaughlin, supra*.

***Conclusion***

Any inquiry concerning this communication or earlier communications from the examiner should be directed to Daniel S. Metzmaier whose telephone number is (571) 272-1089. The examiner can normally be reached on 9:00 AM to 5:30 PM.

If attempts to reach the examiner by telephone are unsuccessful, the examiner's supervisor, Randy P. Gulakowski can be reached on (571) 272-1302. The fax phone number for the organization where this application or proceeding is assigned is 703-872-9306.

Information regarding the status of an application may be obtained from the Patent Application Information Retrieval (PAIR) system. Status information for published applications may be obtained from either Private PAIR or Public PAIR. Status information for unpublished applications is available through Private PAIR only. For more information about the PAIR system, see <http://pair-direct.uspto.gov>. Should you have questions on access to the Private PAIR system, contact the Electronic Business Center (EBC) at 866-217-9197 (toll-free).

  
Daniel S. Metzmaier  
Primary Examiner  
Art Unit 1712

DSM

<b>Notice of References Cited</b>	Application/Control No. 10/088,980	Applicant(s)/Patent Under Reexamination HATCHMAN ET AL.	
	Examiner Daniel S. Metzmaier	Art Unit 1712	Page 1 of 1

**U.S. PATENT DOCUMENTS**

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Name	Classification
	A	US-			
	B	US-			
	C	US-			
	D	US-			
	E	US-			
	F	US-			
	G	US-			
	H	US-			
	I	US-			
	J	US-			
	K	US-			
	L	US-			
	M	US-			

**FOREIGN PATENT DOCUMENTS**

*		Document Number Country Code-Number-Kind Code	Date MM-YYYY	Country	Name	Classification
	N					
	O					
	P					
	Q					
	R					
	S					
	T					

**NON-PATENT DOCUMENTS**

*		Include as applicable: Author, Title Date, Publisher, Edition or Volume, Pertinent Pages)
	U	Hawley's Condensed Chemical Dictionary, Eleventh Edition, edited by Sax and Lewis, Sr. (Van Nostrand Reinhold Company, New York, NY, copyright 1987), pages 1064, 1111-1112, and 1235 (10-1989).
	V	Drew Myers, Surfactant Science and Technology, second edition (VCH Publishers, NY, NY, copyright 1992) pages 46-47 and 118-121 (7-1994).
	W	Milton J. Rosen, SURFACTANTS AND INTERFACIAL PHENOMENA (John Wiley & Sons, New York, NY, copyright 1978) pages 130-133, (05-1983).
	X	

\*A copy of this reference is not being furnished with this Office action. (See MPEP § 707.05(a).)  
Dates in MM-YYYY format are publication dates. Classifications may be US or foreign.

# *Hawley's Condensed Chemical Dictionary*

*ELEVENTH EDITION*

*Revised by*

N. Irving Sax

and

Richard J. Lewis, Sr.

Oct 4 1969

U. S. G. O.



VAN NOSTRAND REINHOLD COMPANY

New York

**sodium isopropylxanthate.** CAS: 140-93-2.

$(\text{CH}_3)_2\text{CHOC(S)SNa}$ .

Properties: Light-yellow crystals soluble in water, deliquescent, decomposes 150C.

Hazard: Moderate fire risk. Irritant to skin and mucous membranes.

Use: Chemical weed killer, fortifying agent for certain oils, ore flotation.

**sodium lactate.** CAS: 72-17-3.

$\text{CH}_3\text{CHOHCOONa}$ .

Properties: Colorless or yellowish syrupy liquid, very hygroscopic, soluble in water, mp 17C, decomposes 140C. Combustible.

Grade: Technical, USP (solution with pH 6.0-7.3).

Use: Hygroscopic agent, glycerol substitute, plasticizer for casein, corrosion inhibitor in alcohol antifreeze.

**sodium-n-lauroyl sarcosinate.**  $\text{C}_{15}\text{H}_{28}\text{NO}_4\text{Na}$ .

Use: Dentrifices, hair shampoos, rug shampoos.

**sodium lauryl sulfate.** CAS: 151-21-3.

$\text{NaC}_{12}\text{H}_{25}\text{SO}_4$ .

Properties: Small white or light yellow crystals, slight characteristic odor, soluble in water, forming an opalescent solution.

Grade: USP, technical, FCC.

Use: Wetting agent in textile industry, detergent in toothpaste, food additive (emulsifier and thickener).

**sodium-lead alloy.** One of several alloys as follows: (1) usually containing 10% sodium and 90% lead, used in the manufacture of lead tetraethyl, (2) containing 2% sodium used as a deoxidizer and homogenizer in nonferrous metals where lead is a component, (3) used as a stabilizer and deoxidizer for lead in cable sheathing.

Hazard: Moderate fire and explosion risk, reacts with moisture, acids, and oxidizing agents.

**sodium lead hyposulfite.** See lead sodium thiosulfate.

**sodium lead thiosulfate.** See lead sodium thiosulfate.

**sodium lignosulfonate.**

Properties: Tan, free-flowing, spray-dried powder, containing 70-80% total lignin sulfonates, balance wood sugars. Combustible.

Use: Dispersant, emulsion stabilizer, chelating agent.

See also lignin sulfonate.

**sodium liothyronine.** (sodium-l-3[4-(4-hydroxy-3-iodophenoxy)-3,5-diiodophenyl]alanine).

$\text{NaOOCCH}(\text{NH}_2)\text{CH}_2\text{C}_6\text{H}_2\text{I}_2\text{OC}_6\text{H}_3\text{IOH}$ .

Properties: Light-tan, odorless, crystalline powder; very slightly soluble in water; slightly soluble

in alcohol; insoluble in most other organic solvents.

Grade: USP.

Use: Medicine (a thyroid hormone).

**sodium MBT.** ( $\text{NaMBT}$ ).  $\text{C}_7\text{H}_4\text{NS}_2\text{Na}$ .

A 50% aqueous solution of sodium mercaptobenzothiazole, light-amber liquid, bulk d 10.5 lb/gal.

Use: Corrosion inhibitor for nonferrous metals, antifreeze, paper mill systems.

**sodium mercaptoacetate.** See sodium thioglycolate.

**sodium-2-mercaptobenzothiazole.** See sodium MBT.

**sodium metabisulfite.** (sodium pyrosulfite).

CAS: 7681-57-4.  $\text{Na}_2\text{S}_2\text{O}_5$ . Chief constituent of commercial dry sodium bisulfite with which most of its properties and uses are practically identical.

Grade: FCC.

Hazard: Toxic by inhalation. TLV: 5 mg/m<sup>3</sup> of air.

Use: In foods, as preservative, lab reagent.

**sodium metaborate.** CAS: 7775-19-1.

$\text{NaBO}_2$ .

Properties: White lumps, d 2.464, soluble in water, mp 966C, bp 1434C. Noncombustible.

Derivation: By fusing sodium carbonate and borax.

Use: Herbicide. Also available commercially as octahydrate and tetrahydrate.

**sodium metanilate.**  $\text{NaSO}_3\text{C}_6\text{H}_4\text{NH}_2$ .

Derivation: The metasodium sulfonate of aniline sold as a solid or 20% aqueous solution prepared by neutralizing metanilic acid.

Grade: Technical, 99%, also 20% solution.

Use: Manufacture of synthetic dyestuffs and drugs.

**sodium metaperiodate.** See sodium periodate.

**sodium metaphosphate.** CAS: 10361-03-2.

$(\text{NaPO}_3)_n$  The value of  $n$  ranges from 3-10 (cyclic molecules) or may be much larger number (polymers). Cyclic sodium metaphosphate, based on rings of alternating phosphorus and oxygen atoms, range from the trimetaphosphate  $(\text{NaPO}_3)_3$  to at least the dexametaphosphate. So-called sodium hexametaphosphate is probably a polymer where  $n$  is between 10 and 20 ("Calgon").

The vitreous sodium phosphates having a  $\text{Na}_2\text{O}/\text{P}_2\text{O}_5$  mole ratios near unity are classified

as sodium metaphosphate. The average number of phosphate groups per molecule in these glasses ranges from 3 to 10. The term sodium metaphosphate is extended to short-chain polymers of the molecules of which the formula is  $\text{Na}_n\text{P}_n\text{O}_{3n+1}$ . These materials are more properly called polyphosphates.

Use: Dental polishing agent, water softening, sequestrant, additives, textile processes.

**sodium metasilicate, anhydrous.**

$\text{Na}_2\text{SiO}_3$ . A crystalline solid.

Properties: Dustless, white powder, total  $\text{Na}_2\text{O}$  content 51.5% (theoretical 48.6%); bulk d 2.6 in water, precipitated by acids and heavy metal ions. Noncombustible.

Derivation: Crystallized from aqueous solution of  $\text{SiO}_2$  at approximately 100C.

Use: Laundry, dairy and food cleaning, base for detergent, deinking aid, deinking paper.

Also available as the pentahydrate. mp 72.2C, total  $\text{Na}_2\text{O}$  in active form 48.6%.

**sodium metavanadate.**  $\text{NaVO}_3$ , often with 4HC.

Properties: Colorless, moist crystals or pale green crystals, mp 630C. Noncombustible. Derivation: Sodium hydroxide in water solution.

Grade: Technical, CP.

Hazard: Toxic by ingestion. Use: Inks, fur dyeing, pH adjuster of plant life, mordants and fixer in gas-scrubbing systems.

**sodium methacrylate.**  $\text{CH}_2=\text{CHCO}_2\text{Na}$ .

Properties: Water-soluble. Use: Resins, chemical intermediates.

**sodium methanearsonate.**

monosodium metanearsonate; sodium metanearsonate; sc.

CAS: 2163-80-6. (CFR 101.101-1).

Properties: White solid, insoluble in water.

Hazard: Toxic by ingestion. Use: Post-emergence herbicide.

**sodium methiodal.** (sodium methiodate). CAS: 126-31-8.

hydrocarbon resins and olefins.

sed for finishing paper from 3 to 12 or the sheet is threaded. e of chilled cast iron mediate rolls, several type. Overall widths erating speeds range ute. The supercalen-thness to high-grade ncoated, as a result al and resilient fiber

paper.

phenomenon in which compounds at tem- perature zero lose both netic permeability, nductivity. Depend- maximum tempera- ) for the phenome- .. Superconductivity etals, noble metals, c metals. It is well- 5, or 7 valence elec- ated with high room- ystem for transmit- ound by, means of been developed.

as that is maintained re (the temperature ured by pressure). s and diffuse more : thus more efficient id chromatography.

h-density polyethyl- ow pressure process. l sheets, film, pipe, nents, etc.

sulfur air-classified sizes, one 93% and 25 US sieve. itches, chrome oxide ck foods, pyrotech- of petroleum; cast- im.

pletely neutral liquid tion of highly active abilizers, soluble in

**"Superloid."**<sup>322</sup> TM for ammonium alginate, a hydrophilic colloid.

Use: Suspending, thickening, emulsifying, and stabilizing agent in creaming and bodying of rubber latex products; protective colloid in resin emulsion paints, adhesives, fire-retarding compositions, ceramics, etc.

**"Superlume."**<sup>248</sup> TM for a super-leveling bright nickel electroplating process on steel stampings, brass, copper, zinc die castings, etc. The materials used are nickel sulfate, nickel chloride, boric acid, and addition agents.

**supernatant.** A liquid or fluid forming a layer on the surface of another liquid.

**superoxide.** A compound characterized by the presence in its structure of the  $O_2^-$  ion. The  $O_2^-$  ion has an odd number of electrons (13) and as a result all superoxide compounds are paramagnetic. At room temperature they have a yellowish color. At low temperature many of them undergo reversible phase transitions accompanied by a color change to white. The stable superoxides are:

sodium superoxide	$NaO_2$
potassium superoxide	$KO_2$
rubidium superoxide	$RbO_2$
cesium superoxide	$CsO_2$
calcium superoxide	$Ca(O_2)_2$
strontium superoxide	$Sr(O_2)_2$
barium superoxide	$Ba(O_2)_2$
tetramethylammonium superoxide	$(CH_3)_4NO_2$

In these compounds each oxygen atom has an oxidation number of  $-1/2$  instead of  $-2$ , as a normal oxide.

**superpalite.** (diphosgene; green cross gas; trichloromethylchloroformate).  $ClCOOCCl_3$ .

Properties: D 1.6525, bp 127.5–128°C.

**"Superpax."**<sup>327</sup> TM for 92–94.5% zirconium silicate with bulk d 68 lbs/cu ft, average particle size 5 microns max.

Use: Ceramic glazes and as a filler for resins and rubbers.

**superphosphate.** (acid phosphate). The most important phosphorus fertilizer, made by the action of sulfuric acid on insoluble phosphate rock (essentially calcium phosphate, tribasic) to form a mixture of gypsum and calcium phosphate, monobasic. A typical composition is  $CaH_4(PO_4)_2 \cdot HOH$  30%,  $CaHPO_4$  10%,  $CaSO_4$  45%, iron oxide, alumina, silica 10%, water 5%.

Typical analysis: Moisture 10–15%, available phosphoric acid (as  $P_2O_5$ ) 18–21%, insoluble phosphoric acid 0.3–2%, total phosphoric acid (as  $P_2O_5$ ) 19–23%.

Grade: Based on available  $P_2O_5$ .

Use: Fertilizer.

See also triple superphosphate and nitrophosphate.

**superphosphoric acid.** See polyphosphoric acid.

**supersaturation.** The condition in which a solvent contains more dissolved matter (solute) than is present in a saturated solution of the same components at equivalent temperature. Such solutions may occur, or can be made, when a saturated solution cools gradually so that nucleating crystals do not form. They are extremely unstable and will precipitate upon addition of even one or two crystals of the solute or upon shaking or other slight agitation. Supersaturated solutions occur in the confectionery industry, e.g., in fudges, maple sugar, etc.

**"Supersheen."**<sup>292</sup> TM for caustic soda solution containing chelating agent and wetting agent. Hazard: Strong irritant to skin and tissue.

Use: Bottle washing and food plant sanitation.

**"Super-sol."**<sup>25</sup> TM for an odorless petroleum naphtha, a rapid-drying, highly purified solvent. Use: Carrier for insecticides, preparation of odorless paints, cleaning compositions.

**"Supralan."**<sup>203</sup> TM for metallized acid colors of good fastness and level dyeing properties.

**"Supramine."** XA.<sup>203</sup> TM for a leather chemical, solubilized sulfur phenol condensate, 75% active.

**"Supranol."**<sup>203</sup> TM for dyestuffs used on wool and silk; good fastness to light, washing, and sea water; can also be used on leather.

**surface.** In physical chemistry the area of contact between two different phases or states of matter, e.g., finely divided solid particles and air or other gas (solid-gas); liquids and air (liquid-gas); insoluble particles and liquid (solid-liquid). Surfaces are the sites of the physicochemical activity between the phases that is responsible for such phenomena as adsorption, reactivity, and catalysis. The depth of a surface is of molecular order of magnitude. The term interface is approximately synonymous with surface, but it also includes dispersions involving only one phase of matter, i.e., solid-solid or liquid-liquid.

See also interface, surface area, surface chemistry.

**surface-active agent.** (surfactant). Any compound that reduces surface tension when dis-



solved in water or water solutions, or which reduces interfacial tension between two liquids, or between a liquid and a solid. There are three categories of surface active agents: detergents, wetting agents, and emulsifiers; all use the same basic chemical mechanism and differ chiefly in the nature of the surfaces involved.

See under above three entries for further information. See also interface, surface chemistry.

**surface area.** The total area of exposed surface of a finely divided solid (powder, fiber, etc.) including irregularities of all types. Since activity is greatest at the surface, that is, the boundary between the particle and its environment, the larger the surface area of a given substance the more reactive it is. Thus reduction to small particles is a means of increasing the efficiency of both chemical and physical reactions; for example, the coloring effect of pigments is increased by maximum size reduction. Carbon black is notable among solids for its huge surface area (as much as 18 acres/lb for some types); the activity of its surface accounts for its outstanding ability to increase the strength and abrasion resistance of rubber. The capacity of activated carbon to adsorb molecules of gases is due to this factor. Surface area is measured most accurately by nitrogen adsorption techniques.

**surface chemistry.** The observation and measurement of forces acting at the surfaces of gases, liquids and solids or at the interfaces between them. This includes the surface tension of liquids (vapor pressure, solubility); emulsions (liquid/liquid interfaces); finely divided solid particles (adsorption, catalysis); permeable membranes and microporous materials; and biochemical phenomena such as osmosis, cell function, and metabolic mechanisms in plants and animals. Surface chemistry has many industrial applications, a few of which are air pollution, soaps and synthetic detergents, reinforcement of rubber and plastics, behavior of catalysts, color and optical properties of paints, aerosol sprays of all types, monolayers and thin films, both metallic and organic. Outstanding names in the development of this science are Graham, Freundlich, and W. Ostwald in the 19th Century, and Harkins, Langmuir, LaMer, and McBain in the 20th. See also colloid chemistry.

**surface tension.** In any liquid, the attractive force exerted by the molecules below the surface upon those at the surface/air interface, resulting from the high molecular concentration of a liquid compared to the low molecular concentration of a gas. An inward pull, or internal pressure, is thus created which tends to restrain the liquid from

flowing. Its strength varies with the chemical nature of the liquid. Polar liquids have high surface tension (water = 73 dynes/cm at 20°C); non-polar liquids have much lower values (benzene = 29 dynes/cm, ethanol = 22.3 dynes/cm), thus they flow more readily than water. Mercury, with the highest surface tension of any liquid (480 dynes/cm) does not flow, but disintegrates into droplets.

See also interface, surface-active agent.

**surfactant.** See surface-active agent.

**"Surfactol."**<sup>202</sup> TM for a series of castor oil-derived, nonionic surfactants.

Use: Emulsifiers, defoamers, plasticizers, solubilizers for oils, dyes, lubricants, in emulsion paints, pigment dispersions, cosmetics, and polishes.

**"Surflo."**<sup>236</sup> TM for a series of bactericides and scale inhibitors. "Surflo-B11" is a film-forming amine that acts as a corrosion inhibitor and bactericide for low pH water-base drilling muds. "Surflo-B33" is a bactericide for treating water-base packer fluids or oil field waters.

**"Surlyn."**<sup>28</sup> TM for a group of ionomer resins. Properties: ("Surlyn" A) Thermoplastic produced as a granular material; flexible, transparent, grease-resistant; very light-weight but tough. Izod impact strength 5.7–14.6 ft-lb/in (higher than any other polyolefin), tensile strength 3,500–5,500 psi, elongation 300–400%, softening point 71°C, insoluble in any commercial solvent, subject to slow swelling by hydrocarbons, to slow attack by acids.

Use: Coatings, packaging films, products made by injection or blow molding, or by thermoforming.

**SUS.** Abbreviation for Saybolt Universal Seconds.

See Saybolt Universal viscosity.

**suspension.** A system in which very small particles (solid, semisolid, or liquid) are more or less uniformly dispersed in a liquid or gaseous medium. If the particles are small enough to pass through filter membranes, the system is a colloidal suspension (or solution). Examples of solid-in-liquid suspensions are comminuted wood pulp in water, which becomes paper on filtration; the fat particles in milk; and the red corpuscles in blood. A liquid-in-gas suspension is represented by fog or by an aerosol spray. If the particles are larger than colloidal dimensions they will tend to precipitate, if heavier than the suspending medium, or to agglomerate and rise to the sur-

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ecipitation.

**wetting agent.** A surface-active agent which, when added to water causes it to penetrate more easily into, or to spread over the surface of, another material by reducing the surface tension of the water. Soaps, alcohols, and fatty acids are examples.

See also detergent.

**WFNA.** Abbreviation for white fuming nitric acid.

See nitric acid, fuming.

**Wharton reaction.** Reduction of  $\alpha,\beta$ -epoxy ketones by hydrazine to allylic alcohols.

**wheat germ oil.** Light-yellow, fat-soluble oil extracted from wheat germ. Dietary supplement. See also tocopherol.

**whey.** The serum remaining after removal of the solids (fat and casein) from milk. Dried whey contains about 13% protein, 71% lactose, 2.3% lactic acid, 4.5% water, and 8% ash, including a low concentration of phosphoric anhydride. Besides its value as an inexpensive source of protein for animal feeds, whey is used as a source of lactose and lactic acid, as well as for the synthesis of riboflavin, acetone, butanol, and fuel-grade ethanol by fermentation processes. Some types of cheese are made from whey and it is also a possible culture medium. Dried whey may be used to replace up to 75% of the polyol component of rigid polyurethane foams. See also lactose.

**whiskers.** Single, axially-oriented, crystalline filaments of metals (iron, cobalt, aluminum, tungsten, rhenium, nickel, etc.), refractory materials (sapphire, aluminum oxide, silicon carbide), carbon, boron, etc. They have tensile strengths of 3-6 million psi and very high elastic moduli. Their upper temperature limit in oxidizing atmospheres may be as high as 1700C and in inert atmospheres up to 2000C. Length may be up to two inches, with diameter up to 10 microns. Their chief use is in the manufacture of composite structures with plastics, glass, or graphite which have many applications in the aircraft and space vehicle field, where their high heat capacity and tremendous strength are invaluable, especially as ablative agents.

**whiskey.**

Properties: Light yellow to amber liquid, d 0.923-0.935 (15.56C), 47-53% alcohol by volume, flash p (CC) 26.6C.

Derivation: Distillation of fermented malted grains (corn, rye, or barley). After distillation whiskey is aged in wooden containers for several

years. The following changes occur during ageing: extraction of wood components (acids and esters), oxidation of the components of the liquid, and reaction between organic compounds in the liquid, forming new flavors.

**Hazard:** Flammable, moderate fire risk. A noncumulative poison, usually harmless in moderate amounts, but may be toxic when habitually taken in large amounts.

**Use:** Beverage, medicine (stimulant, antiseptic, vasodilator).

See also ethanol, proof.

**white acid.** A mixture of ammonium bifluoride and hydrogen fluoride used for etching glass. **Hazard:** Strong irritant to skin and tissue.

**white arsenic.** See arsenic trioxide.

**white copperas.** See zinc sulfate.

**white dye.** An optical bleach or, in general, any substance, such as bluing, which may be added to a white article to increase its apparent whiteness.

**white gasoline.** See gasoline.

**white gold.** Alloy of 90% gold, 10% palladium, or 59% nickel and 41% gold.

**white lead.** Name primarily applied to lead carbonate, basic, but also used for lead sulfate, basic (white lead sulfate) and lead silicate, basic (white lead silicate).

**Hazard:** Toxic by ingestion and skin absorption. Content in paints limited to 0.05% (FDA).

**Use:** Paint pigment.

**white liquor.** See liquor (c).

**white metal.** (1) Any of a group of alloys having relatively low melting points. They usually contain tin, lead, or antimony as the chief component. Type metal, Babbitt, pewter, and Britannia metal are of this group. (2) Copper matte containing about 75% copper, as obtained in copper smelting operations. See copper.

**whitener.** (1) Any of several oil-in-water emulsions in powder form that are dried and concentrated; when added to an aqueous medium they form stable emulsions, giving a white color and a cream-like body to coffee. A typical formulation contains vegetable fat, protein, sugar, corn syrup solids, plus emulsifier and stabilizers. (2) A white pigment or colorant used in the paper and textile industries.

**white oil.** Any of several derivatives of paraffinic hydrocarbons having moderate viscosity, low

**SURFACTANT SCIENCE  
AND TECHNOLOGY**

**Second Edition**

**Drew Myers**

***Adriana Christina and Katrina Alicia -***

**Que sus pasos vayan adelante y se eleven sin dejar sus huellas  
sobre los que transitan el mismo camino.**

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oil have historically been popular and can be found in a number of commercial products.

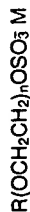
Other sulfated esters of polyols have been suggested as surfactants and have, in fact, been extensively patented. Sulfated monoesters of ethylene glycol<sup>5</sup> and pentaerythritol<sup>6</sup> have received some attention in that regard. They have not, in general, found much commercial acceptance, probably because of the hydrolytic instability of the ester linkage.

The drawbacks of the alcohol esters can be overcome by the use of the alkanolamide linkage. Hydroxyalkylamides can be conveniently prepared by the reaction of hydroxyalkylamines with fatty acids or esters, and by the reaction of epoxides with fatty amides. Since the latter process can result in the formation of a number of products, it is not generally employed for the preparation of materials where a single derivative is desired. The resulting materials are generally more hydrolytically stable than the corresponding ester, with increased stability being obtained if the amide linkage is separated from the sulfate group by more than two carbons. Such materials have been found to have good detergent properties when combined with soaps and are sometimes used in toilet bars and shampoos because of their low irritation.

### Sulfated Ethers

Nonionic surfactants of the polyoxyethylene type, which will be discussed in a following section, generally exhibit excellent surfactant properties. The materials have been found to have two primary disadvantages, however, in that they are not good foam producers and under some conditions give cloudy solutions, which may lead to phase separation. Fatty alcohol sulfates, on the other hand, have good foaming properties (see Chapter Nine), but their more common sodium salts often do not produce clear solutions except at low concentrations. To achieve clarity it is often necessary to use some cation other than sodium, which may increase costs or introduce other difficulties.

When a fatty alcohol is ethoxylated, the resulting ether still has a terminal OH, which can subsequently be sulfated to give the alcohol ether sulfates (AES).

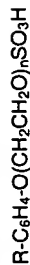


This class of surfactant has shown rapid growth recently because it has the potential to combine the advantages of both the anionic and nonionic surfactant types. In general the ethoxylation of the fatty alcohol is not carried sufficiently far to produce a water soluble nonionic surfactant; usually five or fewer molecules of ethylene oxide are added and the unsulfated material is still of limited solubility in water. The water insoluble nonionic material, however, can then be sulfated with chlorosulfonic acid or  $\text{SO}_3$  and neutralized, usually with sodium hydroxide, to yield the desired product. Other counterions may be employed by slight

modifications of the reaction or by the use of alternative reaction schemes.

The sodium salts of the ether sulfates have very low cloud points, even in relatively high concentration. They do not perform as well as many anionics as wetting agents, but their foaming properties are considerably greater. They have found extensive use in shampoo formulations and, in combination with other anionic and nonionic surfactants, they are being used more for household dishwashing detergents.

Lightly ethoxylated alkylphenols can also be sulfated to produce surfactants with the general formula



The sulfated alkylphenol ethoxylates have found use in toilet soap preparations, but their main success has been in the area of light-duty household detergent liquids. In the preparation of such materials, however, the basic alkyl polyether phenol starting material has two possible reaction pathways: attack at the terminal -OH (to produce the desired sulfated polyether) and sulfonation of the benzene ring. Since the product intended in this case is the sulfated ether, it is desirable that no ring sulfation occur. A complete exclusion of ring attack can be achieved by several techniques, including the use of sulfamic acid as the sulfating agent.<sup>7</sup> Such a procedure produces the ammonium salt, which may in some instances be more useful than the sodium. In most cases, sulfation conditions can be adjusted to minimize any ring substitution.

The figure given for the degree of ethoxylation of an alcohol is only an average. The low values generally used in the products mean that there may be significant quantities of unethoxylated alcohol or phenol left in the mixture, which will be sulfated in subsequent steps and can have a significant impact upon the characteristics of the final product.

### Sulfated Fats and Oils

A final class of sulfated alkyl surfactants is that of the sulfated fats and oils in which the sulfate esters are obtained by the treatment of a variety of hydroxylated or unsaturated natural fats and oils with sulfuric or chlorosulfonic acids. These materials represent the oldest types of commercial synthetic surfactant, dating back to the Turkey red oils referred to earlier. Because of the nature of the starting materials and processes of preparation, the sulfated fats and oils are chemically heterogeneous materials whose properties are very sensitive to their history. In fact, the preparation of such materials may rightly be considered to be more art than science. They will contain not only sulfated glycerides similar to those discussed above, but also sulfated carboxylic acids and hydroxycarboxylic acids produced by hydrolysis of the starting materials. With the increased availability of more chemically pure surfactant materials, the use of the sulfated fatty oils has decreased

Table 3.17. The cmc's of various metal salts of dodecylsulfate.

Counterion	Temperature (°C)	cmc (mM)
Li <sup>+</sup>	25	8.8
Li <sup>+</sup>	40	10.5
Na <sup>+</sup>	25	8.1
Na <sup>+</sup>	40	8.9
K <sup>+</sup>	40	7.8
Cs <sup>+</sup>	40	6.9
(CH <sub>3</sub> ) <sub>4</sub> N <sup>+</sup>	25	5.6
(1/2 Ca <sup>2+</sup> )	54	2.6
(1/2 Mg <sup>2+</sup> )	25	1.6
(1/2 Zn <sup>2+</sup> )	60	2.1

### THE EFFECT OF ADDITIVES ON THE MICELLIZATION PROCESS

Many, if not most, industrial applications of surfactants involve the presence in the solution of cosolutes and other additives that can potentially affect the micellization process through specific interactions with the surfactant molecules (thereby altering the effective activity of the surfactant in solution) or by altering the thermodynamics of the micellization process by changing the nature of the solvent or the various interactions leading to or opposing micelle formation. Examples of specific interactions between surfactant molecules and cosolutes are common when the system contains polymeric materials. Because of the growing importance of such systems, they are treated as a special topic below.

In the absence of specific interactions, which can be quite complex, it is useful to be able to rely upon cmc and aggregation number data determined under a given set of conditions and, aided by theory and whatever empirical relationships may be available, to be able to predict the characteristics of micellization under different conditions. The solution changes commonly encountered that might be expected to impact upon the process include the presence of neutral electrolyte, changes in pH, and the addition of organic materials that may be essentially water insoluble (eg, hydrocarbons), water miscible (short-chain alcohols, acetone, dioxane, etc), or of low water solubility but containing polar groups that impart some surface activity although they are not classified formally as surfactants. In the brief discussion of each category that follows, it must be remembered that each surfactant system can exhibit characteristics different from the general observations noted here.

### Electrolyte Effects on Micelle Formation

In aqueous solution the presence of electrolyte causes a decrease in the cmc of most surfactants, with the greatest effect being found for ionic materials. Nonionic and zwitterionic surfactants exhibit a much smaller effect. For ionic materials, the effect of addition of electrolyte on the cmc can be empirically quantified with the relationship<sup>78</sup>

$$\log_{10} \text{cmc} = -a \log_{10} C_i + b \quad (3-25)$$

where  $a$  and  $b$  are constants for a given ionic head group at a particular temperature, and  $C_i$  is the total concentration of monovalent counterions in moles per liter.

The observed depression of the cmc is primarily due to a reduction in the electrostatic repulsion between head groups and, consequently, a smaller contribution of those groups to the free energy term opposing micellization ( $\Delta G_m^w$ , eq. 3-20). For nonionic and zwitterionic materials, the impact of added electrolyte is significantly less and the relationship in eq. 3-20 does not apply. Shinoda et al.<sup>79</sup> have proposed a relationship of the form

$$\log_{10} \text{cmc} = -K C_s + \text{constant} \quad (\text{for } C_s < 1) \quad (3-26)$$

where  $K$  is a constant for a particular surfactant, electrolyte, and temperature, and  $C_s$  is the concentration of added electrolyte in moles per liter. For alkyl betaines, Tori and Nakagawa<sup>84</sup> found that the value of  $K$  in eq. 3-26 increases with an increase in the length of the hydrophobic chain and with the charge on the anion of the electrolyte.

The observed changes in the cmc of nonionic and zwitterionic materials on the addition of electrolytes cannot, of course, be attributed to the same electrostatic effects as for fully ionic surfactants. The most generally accepted explanation of such effects has been developed in the context of changes in the solvent properties of the aqueous solution for the hydrophobic group. It is well known that the solubility of many materials in water can be significantly altered by the addition of neutral ions. The result of such addition can be a reduced solubility, commonly referred to as "salting out," or increased solubility or "salting in." The specific effect will depend upon the nature of the added electrolyte.

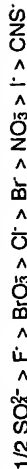
Mukerjee<sup>76</sup> and Ray<sup>81,82</sup> have suggested that the changes in cmc found for nonionic materials with electrolyte addition are related to the amount of work required to disrupt the structure of the aqueous solvent by the insertion of the surfactant molecule. If added electrolyte acts to enhance structure, that is, if it increases the organization of the water molecules through the action of the added ions, the introduction of the monomeric surfactant molecule will require an additional amount of work to overcome that added structural energy. The net result will be a "salting out" of the surfactant and a decrease in the cmc. If, on the other hand, the

added electrolyte acts as a structure breaker, the required work will be less, the surfactant will be "salted in," and the cmc will increase.

In the case of the polyoxyethylene (POE) nonionic surfactants, there exists an additional possible phenomenon that may help to explain the effect of certain cations on their properties.

It is well known, for example, that the cyclic polyoxyethylene or "crown" ethers can form very strong complexes with many appropriately sized ions such as  $\text{Na}^+$  and  $\text{K}^+$ . When the ionic radius of the ion is properly matched to the size of the "basket" formed by the cyclic ether, interactions between the ether oxygens and the ion produce complexes with exceedingly large stability constants. It seems reasonable to expect that linear POE chains of intermediate length, relatively free to assume various configurations in solution, could do so in such a way as to form a "pseudo-crown" ether capable of forming complexes with cationic ions. Should such a phenomenon occur either with the monomer or the micelle, we would expect the overall thermodynamics of the system to be affected, including that of the micellization process. Such a scenario is presently somewhat speculative, but it represents an interesting potential field for further research.

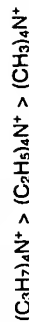
The effectiveness of a given ion at altering the micellization process can be qualitatively related to the radius of hydration of the added ions, with the contribution of the cations and anions being approximately additive. In general, the smaller the radius of hydration of the ion, the greater is its effect on the cmc. The order of effectiveness of anions at decreasing the cmc has been given by Ray and Nemethy<sup>82</sup> as



For cations, the order is



It has been found that the tetraalkylammonium salts of surfactants exhibit an increase in the cmc in the order<sup>82</sup>



### The Effect of pH

Since most modern, industrially important surfactants consist of long-chain alkyl salts of strong acids, it might be expected that solution pH would have a relatively small effect, if any, on the cmc of the materials, an expectation generally borne out by experience. In solutions of sulfonate and sulfate salts, where the concentration of acid or base significantly exceeds that of the surfactant, the excess will act as if it were simply neutral electrolyte with roughly the same results as discussed above.

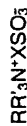
Unlike the salts of strong acids, the carboxylate soap surfactants exhibit a significant sensitivity to pH. Since the carboxylate group is not fully ionized near or below the  $\text{pK}_a$ , the electrostatic interactions between

head groups retarding micelle formation will vary with the solution pH, resulting in changes in the cmc. A similar result will be observed for the cationic alkylammonium salts near and above the  $\text{pK}_a$ , resulting in a decrease in the cmc. When the surfactant is in the ionized form, excess acid or base will act as neutral electrolyte as mentioned above.

It is to be expected that pH will have no effect on the cmc of nonionic surfactants. However, at very low pH it is possible that protonation of the ether oxygen of OE surfactants could occur. Such an event would, no doubt, alter the characteristics of the system. Little can be found in the literature pertaining to such effects, however.

A number of amphoteric surfactant systems show pH sensitivity related to the  $\text{pK}_a$ 's of their substituent groups. At low pH, materials containing carboxyl and amine groups would act as cationic surfactants, while at high pH the activity would be anionic, by analogy to the action of amino acids. If the cation is a quaternary ammonium salt, no pH sensitivity would be expected, as would be the case for a strong acid anionic group. The pH sensitivity of amphoteric surfactants, therefore, will vary according to the specific structure of the materials. The possibilities can be grouped in the following way:

1. Quaternary ammonium/strong acid salt with no significant pH sensitivity



where R is a long-chain alkyl group, R' is a short-chain alkyl, and X is a linking carbon chain usually of one or two carbons.

2. Quaternary ammonium/weak acid, which will be zwitterionic at high pH and cationic below the  $\text{pK}_a$  of the acid



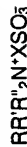
where R, R', and X are as defined in item 1.

3. Amine/weak acid, which will be anionic at high pH, cationic at low pH, and zwitterionic at some pH between the respective  $\text{pK}_a$ 's of the groups



where at least one of R' or R'' is a hydrogen.

4. Amine/strong acid, which will be anionic at high pH and zwitterionic below the  $\text{pK}_a$  of the amine



### The Effects of Added Organic Materials

Organic materials that have low water solubility can be solubilized in micelles to produce systems with substantial organic content where no solubility would occur in the absence of surfactant. The details of the

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# ***Surfactants and Interfacial Phenomena***

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factors: increased oxyethylene content and decreased aggregation number. Other oil-soluble azo dyes similarly show little change in the amount solubilized as the length of the polyoxyethylene chain in nonionics is increased (Mankowich, 1961; Schwuger, 1970). In both nonionic and anionic polyoxyethylenated surfactants the extent of solubilization of Yellow OB is much greater than in sodium alkyl sulfates ( $C_{12}-C_{14}$ ) without polyoxyethylene chains (Tokiwa, 1968). Polymeric quaternary ammonium surfactants made from *n*-dodecyl bromide and poly(2-vinylpyridine) are better solubilizers for oil-soluble azo dyes and for *n*-decanol than monomeric quaternary cationics with similar (monomeric) structures (Tokiwa, 1963; Inoue, 1964). Solubilization of *n*-decanol in the polycationics increased as the alkyl chain content increased to a maximum at 24% alkyl content and resulted, at high decanol content, in intermolecular aggregation of the polycationic molecules (Inoue, 1964).

The introduction into the surfactant molecule of a second ionic head group affords some further insights into the solubilization of polar and nonpolar materials. A comparison of the two series of surfactants, the monosodium salts of the monoesters of maleic acid,  $\text{ROOCC}(\text{H}=\text{CHCOO}^-\text{Na}^+)$ , and the disodium salts of the corresponding monoesters of sulfosuccinic acid,  $\text{ROOCC}(\text{H}_2\text{CH}(\text{SO}_3^-\text{Na}^+))\text{COO}^-\text{Na}^+$ , where  $\text{R} = \text{C}_{12}-\text{C}_{20}$ , shows that the introduction of the sulfonate group into the molecule decreases its solubilizing power for the nonpolar compound *n*-octane and increases its solubilizing power for the polar substance *n*-octyl alcohol (Reznikov, 1966). This may be explained as follows: The introduction of the sulfonate groups increases the hydrophilic character of the surfactant molecule and consequently decreases the aggregation number of the micelles. It also causes increased repulsion between the head groups in the micelles, with consequent increase in the space available for solubilization between the surfactant molecules in the palisade layer. The decreased aggregation number in the micelles causes reduced solubilization of nonpolar substances, whereas the increased repulsion between the head groups results in increased solubilization of polar molecules.

## 2. Structure of the Solubilizate

Crystalline solids generally show less solubility in micelles than do liquids of similar structure, the latent heat of fusion presumably opposing the change. For aliphatic and alkylaryl hydrocarbons, the extent of solubilization appears to decrease with increase in the chain length and to increase with unsaturation or cyclization, if only one

ring is formed (McBain, 1946). For condensed aromatic hydrocarbons the extent of solubilization appears to decrease with increase in the molecular size (Schwuger, 1972). Branched-chain compounds appear to have approximately the same solubility as their normal chain isomers.

For polar solubilizates, the situation is complicated by the possibility of variation in the depth of penetration into the palisade layer of the micelle as the structure of the solubilizate is changed. If the micelle is more or less spherical in shape, we can expect that space will become less available as the micelle is penetrated more deeply. Thus polar compounds that are solubilized close to the micelle-water interface should be solubilized to a greater extent than nonpolar solubilizates that are located in the inner core. This is generally the case, if the surfactant concentration is not high (McBain, 1946; Harkins, 1948; Nakagawa, 1960). We should also expect that polar compounds that are solubilized more deeply in the palisade layer would be less soluble than those whose locus of solubilization is closer to the micelle-water interface. Usually, the less polar the solubilizate (or the weaker its interaction with either the polar head of the surfactant molecules in the micelle or the water molecules at the micelle-water interface) and the longer its chain length, the smaller its degree of solubilization; this may reflect its deeper penetration into the palisade layer. A study of polar dyestuffs, on the other hand, has revealed no correlation between polarity and extent of solubilization (Mankowich, 1959).

## 3. Effect of Electrolyte

The addition of small amounts of neutral electrolyte to solutions of ionic surfactants appears to increase the extent of solubilization of hydrocarbons that are solubilized in the inner core of the micelle and to decrease that of polar compounds that are solubilized in the outer portion of the palisade layer (Klevens, 1950b). The effect of neutral electrolyte addition on the ionic surfactant solution is to decrease the repulsion between the similarly charged ionic surfactant head groups, thereby decreasing the CMC (Chapter 3, Section IV, B) and increasing the aggregation number (Chapter 3, Section III) and volume of the micelles. The increase in aggregation number of the micelles presumably results in an increase in hydrocarbon solubilization in the inner core of the micelle. The decrease in mutual repulsion of the ionic head groups causes closer packing of the surfactant molecules in the palisade layer and a resulting decrease in the volume available there for solubilization of polar compounds.



This may account for the observed reduction in the extent of solubilization of some polar compounds. As the chain length of the polar compound increases, this reduction of solubility by electrolytes appears to decrease and the solubility of *n*-dodecanol is increased slightly by the addition of neutral electrolyte. This is believed to be due to its location deep in the palisade layer close to the locus of solubilization of nonpolar materials (Klevens, 1950b).

The addition of neutral electrolyte to solutions of nonionic polyoxyethylenated surfactants increases the extent of solubilization of hydrocarbons at a given temperature in those cases where electrolyte addition causes an increase in the aggregation number of the micelles. The order of increase in solubilization appears to be the same as that for depression of the cloud point (Section III, A, below) (Saito, 1967):  $K^+ > Na^+ > Li^+$ ;  $Ca^{++} > Al^{+++}$ ;  $SO_4^{--} > Cl^-$ . The effect of electrolyte addition on the solubilization of polar materials is not clear (Mankowich, 1960).

#### 4. Effect of Monomeric Organic Additives

The presence of solubilized hydrocarbon in the surfactant micelles generally increases the solubility of polar compounds in these micelles. The solubilized hydrocarbon causes the micelle to swell, and this may make it possible for the micelle to incorporate more polar material in the palisade layer. On the other hand, the solubilization of such polar material as long-chain alcohols, amines, mercaptans, and fatty acids into the micelles of a surfactant appears to increase their solubilization of hydrocarbons. The longer the chain length of the polar compound and the less capable it is of hydrogen bonding, the greater appears to be its power to increase the solubilization of hydrocarbons, that is,  $RSH > RNH_2 > ROH$  (Klevens, 1949); Shinoda, 1958; Demchenko, 1970). One explanation for this is that the increased chain length and lower polarity result in a lower degree of order in the micelle, with a consequent increase in solubilizing power for hydrocarbons; another is that the additives with longer chain length and lesser hydrogen bonding power are solubilized more deeply in the interior of the micelle, and hence expand this region, producing the same effect as a lengthening of the hydrocarbon chain of the micelle-producing molecule.

On the other hand, the addition of long-chain alcohols to aqueous solutions of sodium dodecyl sulfate decreased its solubilization of oleic acid. The extent of solubilization of the latter decreased as both the concentration and the chain length of the added alcohol increased. These effects are believed to be due to competition

between oleic acid and added alcohol for sites in the palisade layer of the micelle (Matsuura, 1961).

#### 5. Effect of Polymeric Organic Additives

Macromolecular compounds, including synthetic polymers, proteins, starches, and cellulose derivatives, interact with surfactants to form complexes in which the surfactant molecules are absorbed onto the macromolecules, mainly by electrical and hydrophobic interactions. When the surfactant concentration in the complex is sufficiently high, the polymer-surfactant complex may show solubilization power, in some cases greater than that of the surfactant alone, and at concentrations below the CMC of the surfactant (Saito, 1957, 1959; Breuer, 1960; Blei, 1959, 1960; Maruta, 1962). The addition of macromolecules of the proper structure to surfactant solutions can therefore increase the solubilizing power of the latter. Thus sodium alkyl sulfates containing 10 to 16 carbon atoms, at concentrations below their CMCs, form complexes with serum albumin that solubilize oil-soluble azo dyes and isooctane. The moles of dye solubilized per mole of surfactant appear to increase with increase in the chain length of the surfactant, the number of surfactant molecules adsorbed per mole of protein, and the concentration of the protein (Blei, 1959, 1960; Breuer, 1960). The amount of Yellow OB solubilized by sodium dodecyl sulfate-polymer complexes appears to increase with increase in the hydrophobic nature of the polymers (Arai, 1969) and on the addition of small amounts of NaCl (Horin, 1970).

The addition of polyoxyethylene glycols to aqueous solutions of sodium dodecyl sulfate and sodium *p*-octylbenzenesulfonate increased their solubilization power for the azo dye Yellow OB. As the degree of polymerization of the glycol increased, the extent of solubilization for the dye increased. The effect is believed to be due to the formation of two types of complexes between the surfactant micelles and the glycol. Low molecular weight polyoxyethylene glycols (degree of polymerization < 10–15) are believed to form micelle-glycol complexes in which the glycol is adsorbed on the surface of the micelle in a manner similar to that of small polar compounds and the solubilized dye is located mainly in the inner core of the micelle. Higher molecular weight glycols are believed to form true polymer-surfactant complexes in which the glycol is in the form of a random coil bound to the surfactant with its hydrophilic groups oriented toward the aqueous phase. Here the dye is solubilized in the polyoxyethylene-rich region (Tokiwa, 1973b).



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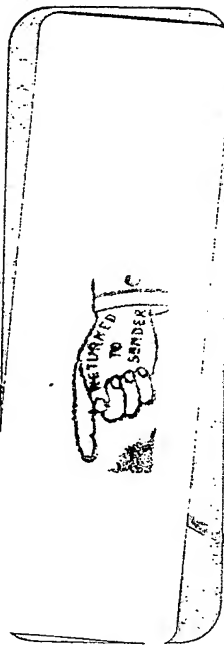
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